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Bis(acetylacetonato)bis(pyrazolato)Ruthenate(III) as a Redox-active Scorpionate Ligand

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The potential of a new anionic octahedral metal complex $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})_2]^-$ ($\mathbf{1}^-$) (pzH = pyrazole) as a ligand with a scorpionate coordination behaviour like tris(pyrazolyl)borate (tp) and reversible redox activity is presented.

Trinuclear metal complexes, $[\text{Ru}^{\text{III}}_2\text{Zn}^{\text{II}}(\text{acac})_4(\text{pz})_4]$ (**2**) and $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}_2(\text{acac})_4(\text{pz})_4]$ (**3**), were each synthesized by the reaction of ZnCl_2 or $\text{Ru}_3(\text{CO})_{12}$ with $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})(\text{pzH})]$ (**1H**) that is in-situ deprotonated and acts as a precursor of $\mathbf{1}^-$. Single-crystal X-ray diffraction studies clarified that $\mathbf{1}^-$ acts as a scorpionate ligand; two $\mathbf{1}^-$ units in **2** and one unit in **3** function as bidentate ligands with two pyrazolates as pincers, while another $\mathbf{1}^-$ unit in **3** functions as a tridentate ligand with one oxygen atom as a tail in addition to the two pyrazolate pincers. Moreover, **2** and **3** showed reversible multi-stage redox behaviours based on the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ couples of the $\mathbf{1}^-$ units in the cyclic voltammetry (CV) measurements. Based on the X-ray, IR, and CV measurements and the comparison with other $\text{Ru}(\text{II})$ complexes with tp derivatives, the $\mathbf{1}^-$ unit was found to act as a redox-active scorpionate with electron withdrawing property compared to the tp.

Introduction

Redox-active ligands have been found to play important roles in metal catalysis used for organic synthesis,[1] artificial water splitting,[2] and biomimetic chemistry,[3] and in the field of molecular based sensors[4] and electronic devices.[4(e), 5] The advantage of redox-active ligands is that the electronic state of the resulting metal complexes could be easily controlled via single/multi electron redox processes compared to time-consuming synthetic modifications. The shift in the HOMO/LUMO level, delocalization of the spin state, or electron storage as a form of radicals in the reaction intermediate are reported to occur followed by redox processes.[6] Dithiolene, catechol, imines, and metallocene-based ligands are representative redox-active ligands that have been investigated in detail,[1, 7] while the synthesis of new redox-active ligands with different electronic properties and coordination behaviors are still challenging themes.[1, 8]

On the other hand, tris(pyrazolyl)borate (tp, Scheme. 1) with no redox-activity is known as a scorpionate ligand that can bind a metal ion with its two pyrazolate units as pincers and even with the third pyrazolate unit as a tail, depending on the conditions.[9] Tp derivatives have been utilized as spectator ligands with almost all metal ions in the periodic table.[9] Therefore, tp derivatives with redox-activity are attractive as ligands with flexible coordination behavior and the ability to tune the electronic state of the resulting metal complexes. The synthetic methods to prepare tp derivatives, including modification/replacement of the pyrazolate ring or replacement of boron with other main group atoms, are generally well reported.[9, 10] As a pioneering study, Wagner and co-workers reported the redox-active scorpionate ligands with ferrocene and *p*-quinone moieties, using the former approach.[11] In contrast, the latter approach of exchanging boron with a redox-active metal ion has not yet been utilized for the synthesis of redox-active scorpionates to the best of our knowledge. Replacing boron with other main-group atoms such as carbon, silicon, and phosphorous has been actively investigated to induce different steric effects and charges from the tp.[10] The use of Zn(II), Pd(II), Re(I), and Pt(II) complexes with pyrazolate ligands as scorpionate-like building blocks for multinuclear complexes and a metal-organic framework (MOF) have also been reported.[12] However, a redox-active transition metal scorpionate is still not yet reported, probably due to the synthetic difficulty of simply exchanging boron in the tp with a redox-active metal ion, maintaining the scorpionate-like coordination behavior.

Scheme 1. Comparison of coordination behaviors of tris(pyrazolyl)borate ($[\text{BH}(\text{pz})_3]^-$) with $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})_2]^-$ (**1**⁻).

In this paper, we demonstrate the ability of an octahedral metal complex $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})_2]^-$ (**1**⁻) (pzH = pyrazole) serve as a redox-active scorpionate ligand. Two pyrazolato ligands and one of the two oxygen atoms in **1**⁻ are expected to act as the pincers and tail, respectively. This octahedral Ru(III) metalloligand is also expected to show a redox behavior based on the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ couples as well as paramagnetic electron spin ($S = 1/2$) and Δ , Λ chirality.[13, 14] We have actually synthesized hetero- and homo-trinuclear metal complexes, $[\text{Ru}^{\text{III}}_2\text{Zn}^{\text{II}}(\text{acac})_4(\text{pz})_4]$ (**2**) and $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}_2(\text{acac})_4(\text{CO})(\text{pz})_4]$ (**3**), by the reaction of $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})(\text{pzH})]$ (**1H**) with ZnCl_2 and $\text{Ru}_3(\text{CO})_{12}$, respectively. The single-crystal X-ray diffraction studies found that the **1**⁻ acts as a bidentate or tridentate ligand in **2** and **3**. The redox chemistry of each trinuclear complex will be discussed based on a comparison with related Ru(II) complexes with tp ligands.

Scheme 2. Synthetic procedures of mononuclear (**1H**, **1H**₂)(PF₆) and trinuclear complexes (**2**, **3**).

Experimental

Materials and physical measurements: $[\text{Ru}(\text{acac})_2(\text{acetonitrile})_2]$ and $[\text{RuCl}_2(\text{dmsO})_4]$ were prepared by following the reported procedures.[15] Acetonitrile for CV measurements was freshly distilled from CaH_2 before use. Other solvents and reagents were purchased from commercial sources and used without further purification. NMR spectra were recorded at 600 MHz with a Bruker AVANCE 600 FT NMR spectrometer. ESI-MS spectrometry was performed with a Exactive Plus (Thermo Fisher Scientific); the mass range was 200–2000 with a nominal resolution (at m/z 200) of 140,000. Elemental analyses were carried out with Perkin Elmer 2400II. UV-vis-NIR and IR spectra were recorded with JASCO V-570 and FTIR-610 spectrometers.

Electrochemical Measurements: Cyclic voltammograms (CVs) were measured in the three electrode cell using a 3 mm diameter glassy carbon working electrode, a platinum auxiliary electrode and a Ag/Ag^+ reference electrode. Measurements were carried out at room temperature using a BAS 610B system. Sample solution was bubbled with Ar for 10 minutes prior to the measurement. The cyclic voltammograms were recorded in 0.1 mol dm^{-3} $^n\text{Bu}_4\text{N}(\text{ClO}_4)/\text{acetonitrile}$ for $[\text{1H}_2](\text{PF}_6)$ and **1H** and in 0.1 mol dm^{-3} $^n\text{Bu}_4\text{N}(\text{ClO}_4)/\text{dichloromethane}$ for **2** and **3** at a scan rate of 0.1 V/s.

Syntheses of $[\text{Ru}(\text{acac})_2(\text{pzH})_2](\text{PF}_6)$ (1H**) and $[\text{Ru}(\text{acac})_2(\text{pz})(\text{pzH})]$ ($[\text{1H}_2](\text{PF}_6)$):** $[\text{Ru}(\text{acac})_2(\text{acetonitrile})_2]$ (0.31 g, 0.80 mmol) and pyrazole (0.11 g, 1.63 mmol) were dissolved into ethanol (20 ml) and refluxed for 2h. After the reaction mixture was cooled to rt, aqueous solution containing NH_4PF_6 (0.66 g, 4.0 mmol) was added and resulting brown solids were filtered. The brown solids were suspended in dichloromethane (100 ml) and filtered. Evaporation of the filtrate afforded brown solids, corresponding to $[\text{Ru}(\text{acac})_2(\text{pz})(\text{pzH})]$ (0.114 g, mol, 33% yield). Meanwhile, filtrate after the addition of NH_4PF_6 was concentrated to the half volume. Appearing Purple solids were collected, filtered, and recrystallized from dichloromethane and hexane. The dark purple microcrystals correspond to $[\text{Ru}(\text{acac})_2(\text{pzH})_2](\text{PF}_6)$ were obtained (71 mg, 15% yield).

$[\text{Ru}(\text{acac})_2(\text{pzH})_2](\text{PF}_6)$ ($[\text{1H}_2](\text{PF}_6)$): ^1H NMR (600 MHz, acetone- d_6): 17.47 (br, 2H), -0.28 (s, 2H), -19.54 (s, 6H), -23.92 (s, 6H), -26.93 (s, 2H), -30.46 (s, 2H), -59.94 (s, 2H). Anal. Calcd (%) for $\text{C}_{16}\text{H}_{22}\text{F}_6\text{N}_4\text{O}_4\text{PRu}$: C, 33.11; H, 3.82; N, 9.65; Found: C, 32.99; H, 3.91; N, 9.73. HRMS (ESI $^+$): calculated for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_4\text{Ru}$ ($[\text{Ru}(\text{acac})_2(\text{pzH})_2]^+$) 436.0679, found 436.0675.

$[\text{Ru}(\text{acac})_2(\text{pz})(\text{pzH})]$ (1H**):** ^1H NMR (600 MHz, acetone- d_6): 6.13 (br, 1H), -0.90 (s, 6H), -13.91 (s, 2H), -15.08 (s, 6H), -25.37 (s, 2H), -31.30 (s, 2H), -33.36 (s, 2H). Anal. Calcd (%) for $\text{C}_{16}\text{H}_{22}\text{F}_6\text{N}_4\text{O}_4\text{PRu}$: C, 44.23; H, 4.87; N, 12.90; Found: C, 44.35; H, 5.11; N, 12.68. HRMS (ESI $^+$): calculated for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_4\text{Ru}$ ($[[\text{Ru}(\text{acac})_2(\text{pz})(\text{pzH})]+\text{H}]^+$) 436.0679, found 436.0683.

Syntheses of $[\text{Ru}_2\text{Zn}(\text{acac})_4(\text{pz})_4]$ (2**):** $[\text{Ru}(\text{acac})_2(\text{pz})(\text{pzH})]$ (0.24 g, 0.55 mmol) was dissolved into a mixed solution of acetonitrile (5 ml) and ethanol (10 ml). To this solution, triethylamine (80 μl) and ethanol solution (5 ml) containing ZnCl_2 (40 mg, 0.29 mmol) were successively added. After the mixture was stirred for 10 min, resulting red solids were filtered, washed by water, and dried in air (224 mg, 83% yield). Single crystals were obtained from benzene and hexane mixed solution.

Anal. Calcd (%) for $\text{C}_{38}\text{H}_{46}\text{N}_8\text{O}_8\text{Ru}_3$ ($[\text{Ru}_2\text{Zn}(\text{acac})_4(\text{pz})_4](\text{C}_6\text{H}_6)$): C, 45.18; H, 4.59; N, 11.10; Found: C, 45.42; H, 4.53; N, 11.10. HRMS (ESI $^+$): calculated for $\text{C}_{32}\text{H}_{41}\text{N}_8\text{O}_8\text{Ru}_2\text{Zn}$ ($[[\text{Ru}_2\text{Zn}(\text{acac})_4(\text{pz})_4]+\text{H}]^+$) 933.0420, found 933.0431.

Syntheses of $[\text{Ru}_3(\text{acac})_4(\text{CO})(\text{pz})_4]$ (3**):** $[\text{Ru}(\text{acac})_2(\text{pz})(\text{pzH})]$ (0.425 g, 0.98 mmol), $\text{Ru}_3(\text{CO})_{12}$ (0.10 g, 0.16 mmol), and triethylamine (150 μl) were added to ethanol (50 ml). After the solution was kept at reflux for 14 h, it was cooled to rt and filtered. The filtrate was evaporated and subjected to silica gel column chromatography (solvent: benzene–benzene/acetonitrile=20/1). Dark-red band that tmainly eluted was collected. Recrystallization from benzene/hexane afforded dark-red crystals (89 mg, 16% yield). Anal. Calcd (%) for $\text{C}_{33}\text{H}_{40}\text{N}_8\text{O}_9\text{Ru}_3$: C, 39.80; H, 4.05; N, 11.25; Found: C, 39.94; H, 4.14; N, 10.97. HRMS (ESI $^+$): calculated for $\text{C}_{33}\text{H}_{41}\text{N}_8\text{O}_9\text{Ru}_3$ ($[[\text{Ru}_3(\text{acac})_4(\text{CO})(\text{pz})_4]+\text{H}]^+$) 998.0134, found 998.0152. $\nu(\text{CO})$: 1953 cm^{-1} (in nujol).

X-ray Crystallography: The crystal structures of $[\text{1H}_2](\text{PF}_6)$, **1H**, **2**, and **3** were determined by the single-crystal X-ray diffraction method. A Bruker APEX II ULTRA (Mo-K α radiation) was used for the data collection. The structures were solved by the direct method using the program *SHELXS-2013*. [16] The refinement and all further calculations were carried out using the program *SHELXL-2013*. [16] All non-H

atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . All H atoms were generated geometrically. Crystallographic and experimental data are summarized in Tables S1, S2 and S3.

Results and Discussion

Ru-pyrazolate mononuclear complexes

$[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})_2]^-$ ($\mathbf{1}^-$) potentially has *trans* and *cis* isomers depending on the position of the two pz^- ligands and corresponds to a di-deprotonated form of $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pzH})_2]^+$ ($\mathbf{1H}_2^+$). Therefore, we first examined the synthetic conditions of *cis*- $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pzH})_2]^+$ ($\mathbf{1H}_2^+$) as a precursor of $\mathbf{1}^-$. As a result, we obtained the cationic complex, *cis*- $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pzH})_2](\text{PF}_6)$ ($\mathbf{1H}_2(\text{PF}_6)$), and unexpectedly neutral complex, *cis*- $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})(\text{pzH})]$ ($\mathbf{1H}$), with 15% and 33% yields, respectively, by the reaction of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{acetonitrile})_2]$ with pyrazole in ethanol under a reflux condition, followed by the addition of NH_4PF_6 (Scheme 2). We considered that the neutral complex $\mathbf{1H}$ is more suitable as a precursor of $\mathbf{1}^-$ than the diprotonated $\mathbf{1H}_2(\text{PF}_6)$. Each complex was characterized by ^1H NMR, ESI-MS, elemental analysis, and single-crystal X-ray diffraction. In the crystal structure of $\mathbf{1H}_2(\text{PF}_6)$, two pyrazole moieties are almost orthogonal and no specific interaction is observed between the two pyrazole ligands (Figure 1). In contrast, the pyrazole and pyrazolato ligands in $\mathbf{1H}$ are almost on the same plane, forming intramolecular hydrogen bond ($\text{H15}\cdots\text{N4}$, $\angle\text{N2-H15}\cdots\text{N4}$: 1.93 Å, 141°). In the electrochemical study, $\mathbf{1H}_2(\text{PF}_6)$ showed two redox couples attributed to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ couples ($E_{1/2} = -0.64, 1.05$ V vs. Fc/Fc^+ , Figure 2), while $E_{1/2}$ of $[\text{Ru}(\text{acac})_3]$ attributed to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ couples are reported to be -1.16 and 0.60 V vs. Fc/Fc^+ in acetonitrile, respectively.[13(d)] Therefore, the positions of the redox couples in $\mathbf{1H}_2(\text{PF}_6)$ are positively shifted ($0.45\sim 0.52$ V) compared to those of $[\text{Ru}(\text{acac})_3]$, indicating that the ruthenium center in $\mathbf{1H}_2(\text{PF}_6)$ is in the electron deficient state compared to that of $[\text{Ru}(\text{acac})_3]$. In the case of $\mathbf{1H}$, it showed irreversible peaks at -0.67 and 0.59 V vs. Fc/Fc^+ in addition to the reversible redox couples at -1.08 and 1.05 V vs. Fc/Fc^+ . We consider that the irreversible and reversible redox couples mainly originated in the deprotonated pyrazolato ligand and ruthenium center, respectively, however, the detailed mechanism of the irreversible redox is still unclear. The $E_{1/2}$ of the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple in $\mathbf{1H}$ (-1.08 V vs. Fc/Fc^+) was observed at a position close to that of $[\text{Ru}(\text{acac})_3]$, indicating that the metal center in $\mathbf{1H}$ is electron-rich compared to that of $\mathbf{1H}_2^+$. Therefore, the di-deprotonated form $\mathbf{1}^-$ was expected to be a more electron rich state than $\mathbf{1H}$ and to act as a ligand.

Figure 1. ORTEP representations of (a) $\mathbf{1H}_2(\text{PF}_6)$ and (b) $\mathbf{1H}$ (PF_6^- was omitted for clarity. Ellipsoids are 50% probability level).

Figure 2. Cyclic voltammograms of (a) $\mathbf{1H}_2(\text{PF}_6)$, (b) $\mathbf{1H}$, (c) $\mathbf{2}$, (d) $\mathbf{3}$. Measurements of $\mathbf{1H}_2(\text{PF}_6)$ and $\mathbf{1H}$ (1 mM) were done in CH_3CN , while $\mathbf{2}$ and $\mathbf{3}$ (1 mM) were measured in CH_2Cl_2 . In every scan, $[\text{Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) was used as the electrolyte and the scan rate was 0.1 V s^{-1} .

Formation of trinuclear complexes

$\mathbf{1H}$ was expected to be deprotonated in-situ and act as a precursor of $\mathbf{1}^-$. In fact, the trinuclear complex $[\text{Ru}^{\text{III}}_2\text{Zn}^{\text{II}}(\text{acac})_4(\text{pz})_4]$ ($\mathbf{2}$) was obtained with 83% yield from the reaction of $\mathbf{1H}$ with ZnCl_2 in ethanol at ambient temperature. $\mathbf{2}$ consists of the two $\mathbf{1}^-$ units and Zn^{II} ion ($\mathbf{2} = [\text{Zn}^{2+}(\mathbf{1}^-)_2]$). The NMR spectra of $\mathbf{2}$ measured in acetone- d_6 in the range from -50 °C to rt were very broad compared to those of the paramagnetic mononuclear $\text{Ru}(\text{III})$ complexes with acac ligands such as $[\text{Ru}(\text{acac})_3]$ and $[\text{Ru}(\text{acac})_2(\text{L})]$ (L is a monodentate ligand) (Fig S5),[13] probably due to the dissociation equilibrium with the di- or mononuclear complexes. The formation of the trinuclear structure in solution was confirmed by high resolution ESI-MS spectrometry (Fig S3). A single-crystal X-ray diffraction study found that $\mathbf{2}$ has the chiral Δ - Δ or Λ - Λ configuration, while the meso form was not detected under this synthetic condition.

We further examined the coordination behavior of $\mathbf{1H}$ for an inert ruthenium ion. $[\text{Ru}_3(\text{CO})_{12}]$ and $[\text{RuCl}_2(\text{dmsO})_4]$ (dmsO = dimethylsulfoxide) were examined as the precursors of a ruthenium ion, while ethanol was used as the solvent like the case of $\mathbf{2}$. A triruthenium complex $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}_2(\text{acac})_4(\text{CO})(\text{pz})_4]$ ($\mathbf{3}$) was obtained with 16% yield from the reaction of $\mathbf{1H}$ and $[\text{Ru}_3(\text{CO})_{12}]$ in ethanol at reflux for 14 h, followed by silica-gel column chromatography (benzene/acetonitrile = 20/1). $\mathbf{3}$ consists of the two $\mathbf{1}^-$ and $\text{Ru}^{\text{II}}\text{CO}$ moieties ($\mathbf{3} = [\text{Ru}(\text{CO})(\mathbf{1}^-)_2]$). $\mathbf{1H}$ was found to act as a precursor of $\mathbf{1}^-$ even under a reflux condition. We

also examined the reaction of **1H** and $[\text{RuCl}_2(\text{dmsO})_4]$ in the presence of AgNO_3 in ethanol at reflux for 18 h. The ESI-MS measurement of the crude product indicated the presence of the cationic complex $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pzH})_2]^+$. Moreover, no ruthenium complexes eluted in the following silica gel column chromatography with benzene/acetonitrile = 10/1 as an eluent. This result indicates that the CO ligand stabilizes the trinuclear structure of **3**. The Characterization of **3** was performed by ESI-MS, elemental analysis, and single-crystal X-ray diffraction. The central ruthenium with CO was assigned to the divalent state. **3** has the Δ - Λ configuration, while the Δ - Δ and Λ - Λ forms could not be isolated under this synthetic procedure.

2 and **3** showed similar UV-vis absorption in the range from 300 to 600 nm, while only **3** showed a broad and weak absorption in the range from 600 to 1000 nm (Figure 3). The weak absorption from the visible to NIR region in **3**, which was not observed in $[\text{1H}_2](\text{PF}_6)$ and **1H**, might indicate a weak electronic communication between the RuCO moiety and either or both of the 1^- units in **3**, while further theoretical calculation is necessary for detailed discussion. In this paper, the electronic interaction is discussed based on the electrochemical studies in the following section.

Figure 3. UV-vis spectra of (a) $[\text{1H}_2](\text{PF}_6)$, (b) **1H**, (c) **2**, (d) **3**. All measurements were carried out in acetonitrile.

The trinuclear structures of **2** and **3** were finally clarified by single-crystal X-ray diffraction (Figure 4, Table S3). In **2**, two 1^- units coordinate to the Zn(II) ion as bidentate ligands with the two pyrazolates. Coordination geometries of the Zn(II) are almost consistent with those of the tetrahedral Ni(II) and Zn(II) complexes with tp derivatives (Tables S1 and S2),^[17] while the N4–Zn1–N5 angle ($137.9(2)^\circ$) opens from a regular tetrahedron. Moreover, two oxygen atoms, each belonging to different 1^- units, are relatively near the Zn(II) (Zn \cdots O4: 3.118(5) Å, Zn \cdots O5: 3.107(5) Å). Acetylacetonato is sometimes known to work as a bridging ligand as in the cases of $[\text{Co}(\text{acac})_2]$ and $[\text{Ni}(\text{acac})_2]$ that have oligomeric structures in the solid state.^[18] Although the Zn \cdots O lengths in **2** are clearly longer than the M \cdots O lengths observed in $[\text{Co}(\text{acac})_2]$ and $[\text{Ni}(\text{acac})_2]$ (2.15–2.40 Å),^[18] the O atoms in the second coordination sphere are indicated to stabilize the distorted coordination geometry of the Zn ion. Steric interactions between the two 1^- units are also observed. One acac (O5, O6, C23–C27) moiety stacks parallel to another acac (O3, O4, C6–C10); the distance between the H27 belonging to C23 and C9 is 3.228 Å. This steric interaction is the probable reason that **2** has the Δ - Δ or Λ - Λ configuration.

In **3**, one 1^- unit acts as a bidentate ligand like those in **2**, while another unit acts as a tridentate ligand (Figure 4). The tridentate 1^- unit is closely positioned to the RuCO unit: Ru1–Ru2: 3.3627(3) Å and Ru2–Ru3: 3.9617(3) Å. The Ru2–O4 distance of 2.235(4) Å at 120 K is consistent with the M–O distances in $[\text{Co}(\text{acac})_2]$ and $[\text{Ni}(\text{acac})_2]$. That is, the O atom (O4) of the acac ligand is regarded to completely coordinate to the central ruthenium. At the trans position, one CO coordinates to the ruthenium, forming an octahedral geometry. Both Ru–C and C–O distances (Ru2–C17: 1.809 (8) Å and C17–O5: 1.151 (9) Å at 120 K) are slightly shorter among the Ru(II) complexes with CO ligands.^[19] The short Ru2–C17 distance indicates the strong Ru–C bond, reflecting the weak bonding between the Ru and O atom at the trans position. In contrast, the short C17–O5 distance indicates the weak π -back donation from the ruthenium to CO. The CO stretching band in **3** was observed at 1953 cm^{-1} , while $\nu(\text{CO})$ in several mononuclear Ru(II) complexes with CO and Tp ligands are reported at slightly lower wavenumbers;^[20] for example, $\text{TpRu}(\text{CO})(\text{R})(\text{PPh}_3)$ (R = H, Me, Et, Pr, or Ph) is reported to show $\nu(\text{CO})$ in the range of 1916 – 1928 cm^{-1} .^[20(a)] Although the quantitative comparison is difficult due to the contribution of other monodentate ligands (R, PPh₃) to $\nu(\text{CO})$ in the above mononuclear complexes, the higher $\nu(\text{CO})$ frequency of **3** is qualitatively consistent with the proposed weak π -back donation. The weak π -back donation further indicates that Ru2 is electron deficient due to the electron withdrawing from the 1^- units. The crystal structures of **2** and **3** show that 1^- actually acts as a scorpionate ligand, bidentate or tridentate, depending on the conditions, whereas it is difficult to judge whether the Ru2–O4 bond is maintained in solution.

Figure 4. ORTEP (50% probability level) representations of (a) **2** and (b) **3**.

Electrochemical studies of **2** and **3**

The cyclic voltammetry (CV) measurement of **2** showed four reversible redox couples at -1.42 , -1.24 , 0.54 , 0.71 V vs. Fc^+/Fc , which are attributed to the $\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$, $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$, $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}$, and $\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}/\text{Ru}^{\text{IV}}\text{Ru}^{\text{IV}}$ couples, respectively (Figure 2). The comproportionation constant (K_c) for the mixed-valence states of $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}$ at $T = 295$ K are calculated to be $10^{3.1}$ and $10^{2.9}$, respectively. These values are appropriate compared to other dinuclear ruthenium(III) complexes such as $[\{\text{Ru}(\text{acac})_2\}_2(\text{tae})]$ ($\text{tae} = 1,1,2,2$ -tetraacetylcethanate dianion) with the K_c values of $10^{3.0}$ and $10^{2.0}$ for the $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}$ states in dichloromethane, respectively.[13(c)] Based on the K_c values, the through-bond electronic interaction between the two 1^- units in **2** is indicated to be weak. The magnetic study of **2** also indicated the weak or no specific magnetic interaction between the two paramagnetic 1^- units ($S = 1/2$). The fitting of the χ -T plot of **2** based on the Bleaney-Bowers equation indicated almost no magnetic interaction between the 1^- units (Figure S6).

In **3**, the central ruthenium(II) (Ru_c) is also redox-active in addition to the two peripheral ruthenium(III) ions. The four reversible redox couples at -1.31 , -1.02 , 0.50 , 0.84 V vs. Fc^+/Fc are formally attributed to the $\text{Ru}^{\text{II}}\text{Ru}_c^{\text{II}}\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}\text{Ru}_c^{\text{II}}\text{Ru}^{\text{III}}$, $\text{Ru}^{\text{II}}\text{Ru}_c^{\text{II}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}\text{Ru}_c^{\text{II}}\text{Ru}^{\text{III}}$, $\text{Ru}^{\text{III}}\text{Ru}_c^{\text{II}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}\text{Ru}_c^{\text{III}}\text{Ru}^{\text{III}}$, and $\text{Ru}^{\text{III}}\text{Ru}_c^{\text{III}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}\text{Ru}_c^{\text{III}}\text{Ru}^{\text{IV}}$ couples, respectively (Figure 2). The redox couple at -1.02 (vs. Fc^+/Fc) in **3** and that at -1.24 (vs. Fc^+/Fc) in **2** are both mainly attributed to the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ couple of one 1^- unit. The difference in the potentials (0.22 V) indicates that the 1^- unit in **3** is in an electron-rich state compared to that in **2**. That is, electron donation from the Ru_c to at least one 1^- unit is indicated in **3**. The K_c value for the $\text{Ru}^{\text{II}}\text{Ru}_c^{\text{II}}\text{Ru}^{\text{III}}$ state in **3** is $10^{4.9}$, which is higher than that for the $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ mixed-valence state in **2**, showing that the mixed valence state in **3** is more stabilized through electronic communication between the Ru_c and at least one 1^- unit. Moreover, the redox couple at 0.50 V (vs. Fc^+/Fc) in **3** is formally attributed to the $\text{Ru}_c^{\text{II}}/\text{Ru}_c^{\text{III}}$ couple, whereas the oxidation potentials ($E_{1/2}$) of the $[\text{Ru}^{\text{II}}(\text{tp})_2]$ complexes with various substituents are reported in the range from -0.1 to 0.1 V (vs. Fc^+/Fc).[21] The difference in the potentials also indicates that the Ru_c is in an electron deficient state compared to the ruthenium in the $[\text{Ru}^{\text{II}}(\text{tp})_2]$ derivatives. This result is also consistent with the results of the X-ray and IR measurements. The electron-withdrawing ability of 1^- is an interesting feature as a scorpionate ligand for synthesizing metal complexes with a unique coordination geometry and reactivity.[22]

Conclusions

$[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pz})_2]^-$ (1^-) was clarified to act as a redox-active scorpionate ligand with the two pyrazolates and one oxygen atom as the pincers and the tail, respectively. The trinuclear complexes, $[\text{Ru}^{\text{III}}_2\text{Zn}(\text{acac})_4(\text{pz})_4]$ (**2**) and $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}_2(\text{acac})_4(\text{CO})(\text{pz})_4]$ (**3**), were actually synthesized from the reaction of ZnCl_2 or $\text{Ru}_3(\text{CO})_{12}$ with **1H** that acts as the precursor of 1^- . The two 1^- units in **2** behave as bidentate ligands, while the two 1^- units in **3** behave as bidentate and tridentate ligands, respectively. The X-ray, IR, and CV studies show that the 1^- unit has an electron withdrawing property compared to tris(pyrazolyl)borate. As a result, the central ruthenium(II) ion in **3** was indicated to be in an electron deficient state compared to the $\text{Ru}(\text{II})$ complexes formed with two tp ligands. The anionic metal complex 1^- was clarified to act as the scorpionate ligand with a redox-activity and unique electron withdrawing property, which is an interesting feature for future applications as metal catalysts.

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Notes and references

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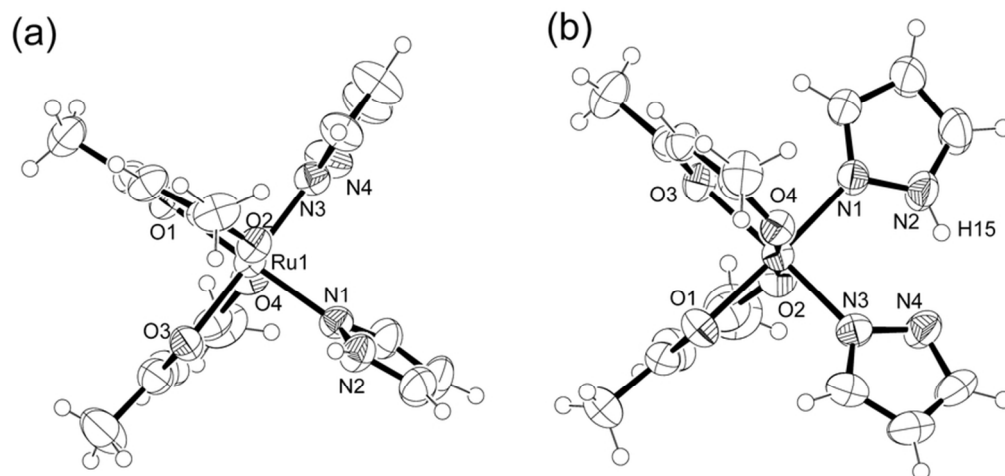
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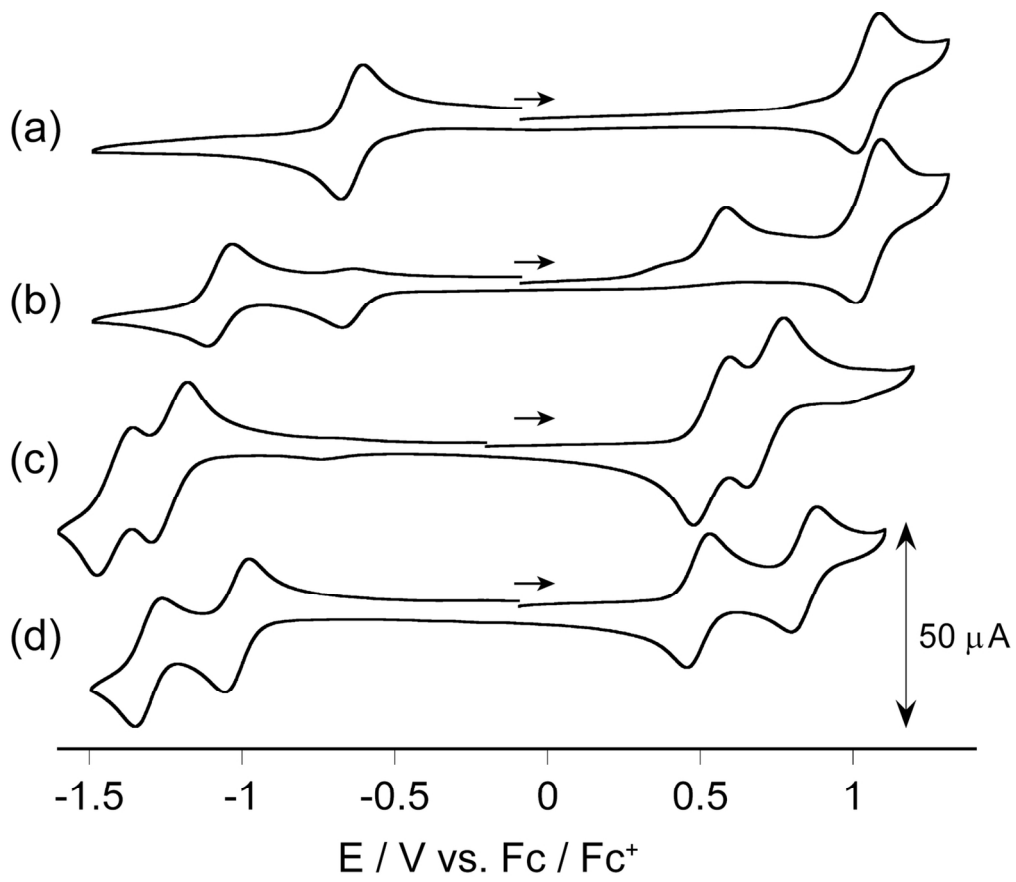
† Electronic Supplementary Information (ESI) available: [ESI-MS spectra, NMR spectra, SQUID data, crystal data, and X-ray crystallographic file in CIF format (CCDC 1016235-1016237, 1016239]. See DOI: 10.1039/b000000x/

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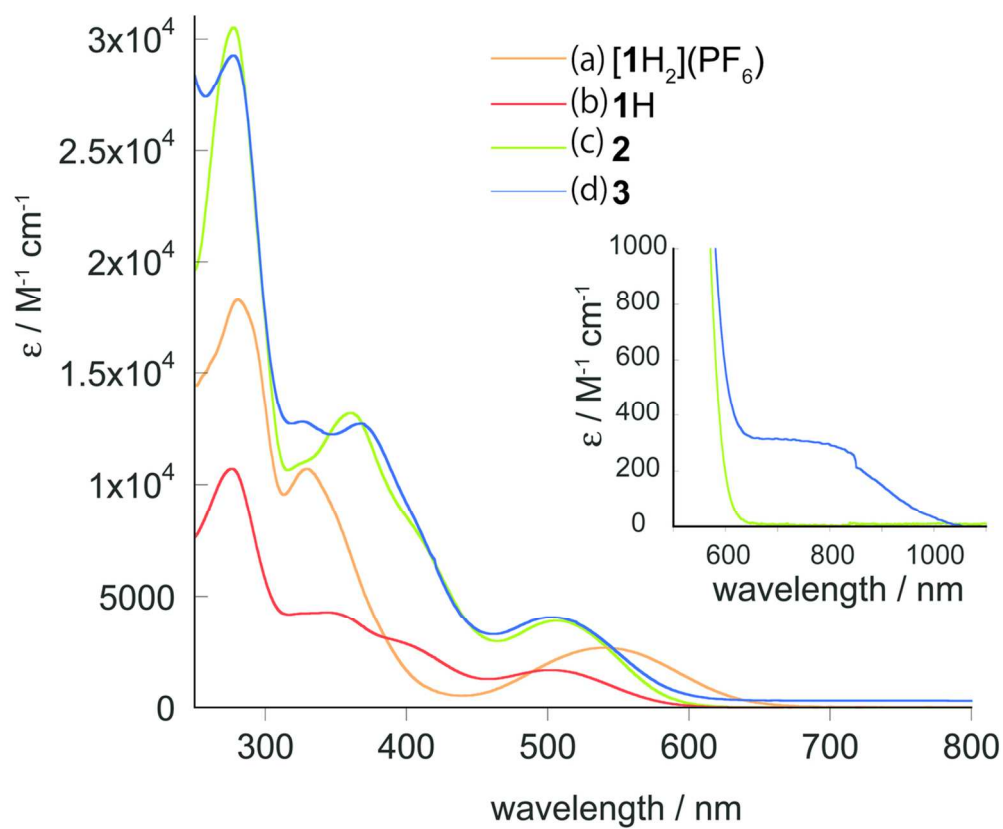
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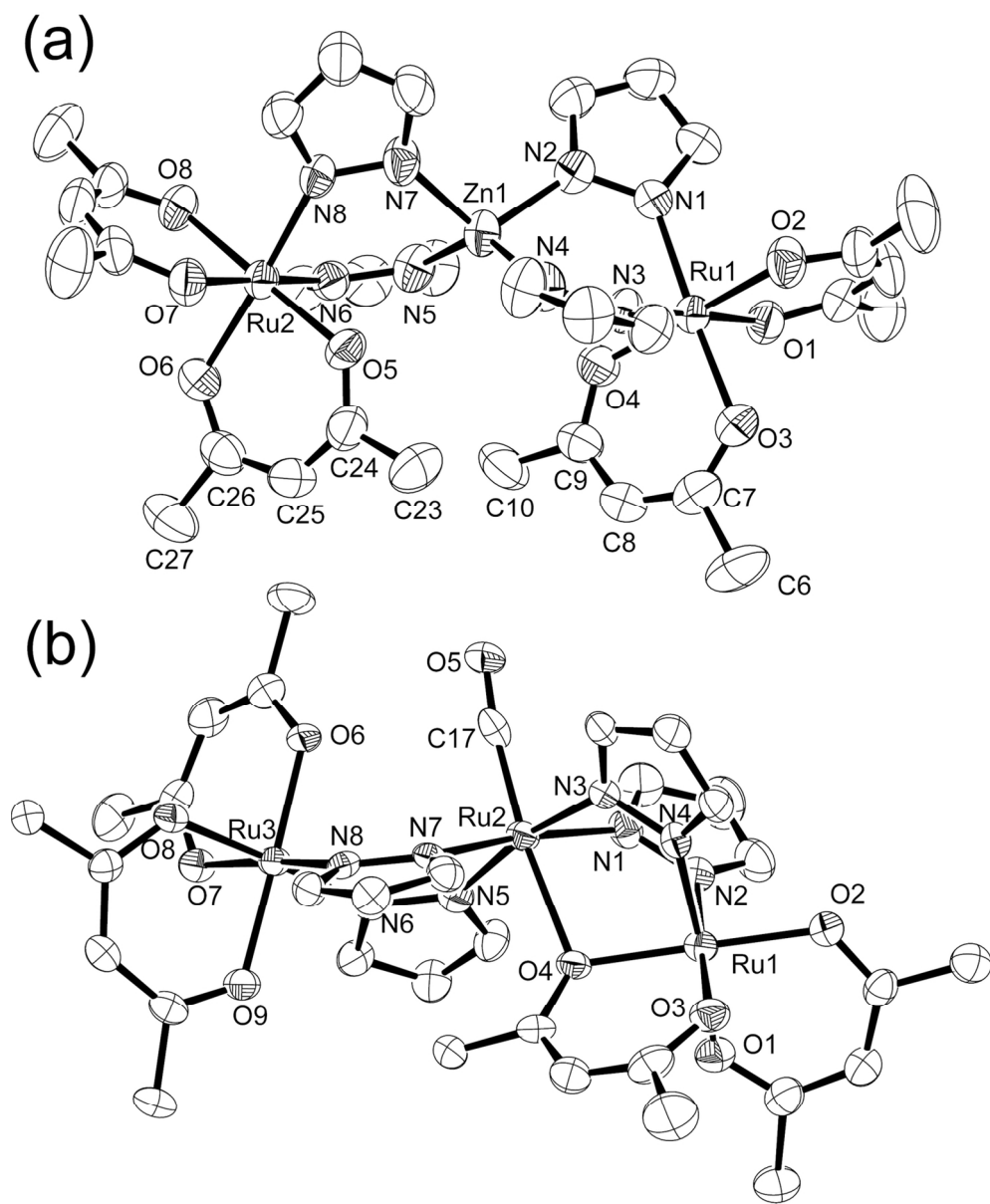
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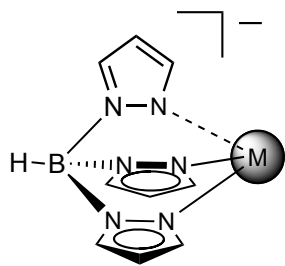
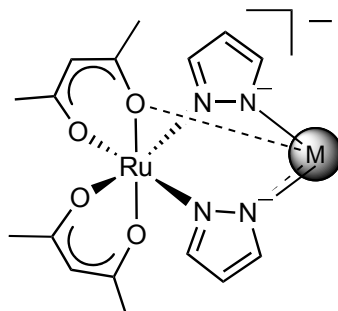
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 $[\text{BH}(\text{pz})_3]^- (\text{tp})$  $[\text{Ru}(\text{acac})_2(\text{pz})_2]^- (\mathbf{1}^-)$

